Enhanced Hydrophilic Polyurethane Prepolymers for Consumer and Industrial Applications

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DOW

Exhibit B

Abstract

Polyurethanes are one of the most complex and varied families of polymers, their greatest advantage being their extreme versatility, both in finished product properties and in unique processing characteristics, as well as in ease of production and application. Thanks to the versatility of polyurethane chemistry, it is possible to manufacture products that are suitable for use in a large variety of specialized applications. This study describes a family of specially tailored polyurethane prepolymers that can be used in the manufacture of products having particularly high hydrophilicity, improved softness and high breathability properties. Dow successfully commercializes these hydrophilic polyurethane prepolymers under the trademark HYPOL*.
HYPOL* hydrophilic prepolymers are suitable for use in a large variety of consumer and industrial applications, where they can be applied as foamed or non-foamed derivatives. Thanks to their molecular architecture, HYPOL* prepolymers feature advantages, such as controlled reactivity profile and low energy requirements for easier processing. Items based on HYPOL* prepolymers show outstanding hydrophilicity in their ability to hold up to twenty times their weight in aqueous liquid.
This study describes the recent developmental work made by Dow Polyurethane Systems business, aimed at further enhancing the level of performance offered by HYPOL* prepolymers. The objective was to meet the ever-increasing number of customer needs, and thus to increase the use of hydrophilic prepolymers in diversified existing as well as new specialized applications. Due to the wide variety of specific market needs as well as particular application requirements, these research and development activities were performed aiming at satisfying specific customer unmet needs. Lower viscosity, lower freezing points, and improved physical-mechanical properties are among the features that characterize these recently developed enhanced hydrophilic prepolymer grades.

Introduction

During the middle 1970's, a team led by Dr. Clifton L. Kehr developed the basis for the first generation of commercially available Hydrophilic Polyurethane Prepolymers. These tailored prepolymers have set the hydrophilic foams and gels industry standards in many diverse applications, from mechanical and acoustical dampening to moisture management areas, to consumer products. Dow successfully commercializes these prepolymers under the trade name HYPOL*.

HYPOL* prepolymers are unique reactive liquids derived from the reaction of polyols and diisocyanates. The pre-reacted building blocks of the prepolymer allow better design and definition of the molecular architecture and of the physical mechanical properties of the final product. Compared with the diisocyanate raw materials, processing with prepolymers has several advantages:

- Improved handling and compatibility of the reaction components;
- Better control of viscosity, polymeric structure and reactivity;
- Lower levels of diisocyanates as pure raw material and;
- Maximization of ease of application.

Low exotherms are generated during the

TABLE N° 1

TYPICAL PROPERTY	HYPOL* 2000	HYPOL* 2002	HYPOL* 3000	HYPOL* 2060G	HYPOL* G50
% NCO	6.6	6.6	9.0	3.5	7
Base Diisocyanate	TDI	TDI and MDI	TDI	TDI	IPDI

foaming reaction when compared to conventional PU. This feature makes HYPOL* systems an excellent choice to incorporate temperature sensitive materials directly into a polyurethane foam or gel structure.
The foams and gels obtained by the reaction of HYPOL* prepolymers and the curative phase will exhibit high levels of hydrophilicity. Foams typically will absorb 20 to 30 times their own weight in water. Solid HYPOL* based hydrogels can contain as much as 95% water in their composition.
Both the foams and gels will release water through evaporation, shrinking in the process. Upon re-wetting, they will re-absorb liquids.

How do HYPOL* Prepolymers work?

HYPOL* prepolymers are unique reactive liquids which simply require the addition of an active hydrogen containing compound to produce hydrophilic foams and gels. The compounds that can be used include, for example, alcohols, amines and water.
Any additive or active ingredient that can be incorporated into the reactant phase (in solution, suspension, emulsion, etc.) may be introduced directly into the foam or gel matrix during the processing step. The resultant foams or gels will have specific activity and characteristics or provide controlled release of an active ingredient.
HYPOL* based foams and gels are usually produced using specially modified low-pressure mix metering equipment. The prepolymer and the reactant phase are pumped simultaneously into a dynamic mixing head. The reacting mixture is then poured into molds, conveyor belts, or onto a casting line. The polymerization process usually will take 5 - 10 minutes.
In gel processing, the prepolymer is usually mixed with the curative phase at ratios that vary from one part prepolymer to ten curative or one to twenty. As the reaction proceeds, the viscosity builds up with minimum volume expansion before setting into a solid gel. Using gel-forming prepolymers, solid hydrogels can be produced containing as much as 95% water. By using a lower amount of curative it is possible to prepare foamed products with densities ranging from about 60 Kg/m³ (4 pcf) up to about 160 Kg/m³ (10 pcf).

Areas of application

The versatility of HYPOL* prepolymers makes them suitable for a variety of applications. HYPOL* based foams and gels can be produced in the form of molded or slab, cast sheets, or as coatings as described below.

Consumer:
The softest PU foams can be obtained by reacting HYPOL* prepolymers with the proper curative phase. These super-soft foams have set the standards as the foams of choice for cosmetic and make-up applications.
Reticulated foams, sea sponge-like, are obtained by the proper choice of HYPOL* and the corresponding curative phase. The reticulation process doesn't require the addition of Auxiliary Blowing Agents (ABA).
Different grades of foams can be loaded with soaps, perfumes, or abrasive materials for house hold applications.
HYPOL* prepolymers can be used to bind materials such as non-wovens, with a middle PU foam layer that can contain different components as previously described.

Vibration & Acoustical Dampening:
HYPOL* systems are the leading materials for the production of slow recovery (or dead) foams. The ability to dial-in the recovery time, the cell size, and the level of softness, make them an optimal choice for applications such as vibration reduction, acoustical dampening pads, and comfortable earplugs.

Moisture Management:
Used as coatings and adhesives, HYPOL* prepolymers provide a dynamic solution to laminate and coating requirements where the breathability of items such as clothing or high water absorbency of foam pads is important for a fast dissipation or retrieval of moisture.

Horticulture:
Horticulturists have discovered the benefits of HYPOL* as hydrophilic binders for growing media that will support tender plants' roots. Time and cost savings, along with increase yield in operations performance via equipment automation, are achievable.

Hydrogels:
HYPOL* prepolymers can produce opaque or clear gels. The gels can contain high levels of water content featuring enhanced elasticity and greater stability. These features are particularly useful for the increasingly innovative packaging designs required by global consumer markets where functionality and aesthetics are key issues.
HYPOL* based hydrogels will feature the slow release of water along with functional additives that have been trapped in the gel matrix.
High tech applications such as bio-support systems, whereby the final product will feature entrapment of enzymes, proteins and other biologic materials, find HYPOL* prepolymers as the material of choice.

Objectives

As the product line based on HYPOL* prepolymers was added to the current commercial offering of Dow's Polyurethane Systems business, the R&D laboratories and Application Development groups have been working to further enhance the hydrophilic polyurethane technology to best satisfy increasing customer needs.
Dow Polyurethane Systems business is focusing its developmental work on:

- The improvement of the foam mechanical properties when fully saturated with water. The current PU based hydrophilic foams exhibit low physical properties when subject to mechanical stress and forces while fully wet.
- The development of prepolymers with lower solidification temperature and lower viscosity. The current foam forming HYPOL* prepolymers will start to solidify below 20°C (68°F).

To address the above issues, a new series of prepolymer grades has already been defined with the typical properties outlined in Table 2.

TABLE N° 2

Property	HYPOL* DEV 1 Prepolymer	HYPOL* DEV 2 Prepolymer
% NCO	6	9
Base Diisocyanate	TDI	TDI
Application	Hydrophilic foams	Hydrophilic foams

Experimental

Side to side comparisons were made using the following products:

- HYPOL* 2000 Prepolymer commercially available grade.
- Foam forming developmental grades HYPOL* DEV 1 and DEV 2 Prepolymers.

Foam Preparation:
Supersoft foams were prepared in the laboratory by reacting the prepolymers described below with the proper curative phase under the conditions listed in Table 3.

Foams conditioning:
Foams were soaked under regular tap water for 30 minutes.
Immediately after the wet foams were weighed to obtain the saturated weight values.
The excess water was then squeezed out of the foams to obtain the water retention values and for physical properties testing.

Water holding capacity (WHC):
Number of times the foam can hold its original weight in water.

Formula:
WHC = Weight of foam saturated with water/Dried foam weight

% Water Retention (%WR): Percentage of water retained by the foam matrix after excess water removal.

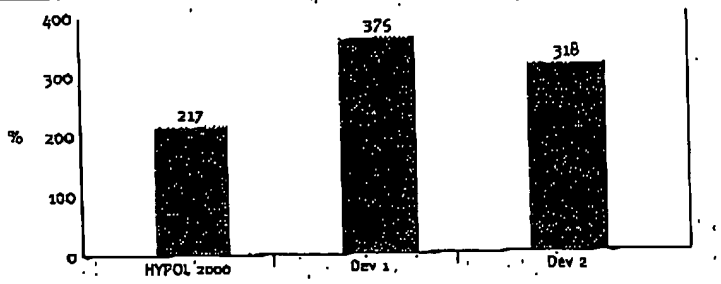
Formula:
%WR = (Weight of wet foam - Dried weight)/Dried weight

FIGURE 1. WATER HOLDING CAPACITY

TABLE N° 3

Item	HYPOL* 2000 Prepolymer	HYPOL* DEV 1 Prepolymer	HYPOL* DEV 2 Prepolymer
Mechanical mixer (RPM)	1000	1000	1000
Cream time (seconds)	20	20	20
Tack-free time (minutes)	3	3	3

FIGURE 2. WATER RETENTION



Physical testing:
Test specimens were placed in a forced convection oven to bone dry at 70°C (158°F) for 4 hours, then they were allowed to stabilize at room temperature overnight prior to testing.
For the wet testing, the specimens were soaked under regular tap water for 30 minutes. Immediately after the excess water was squeezed out of the foams. The specimens were tested at their maximum percentage of water retention as detailed in Figure 2.

TABLE N° 4

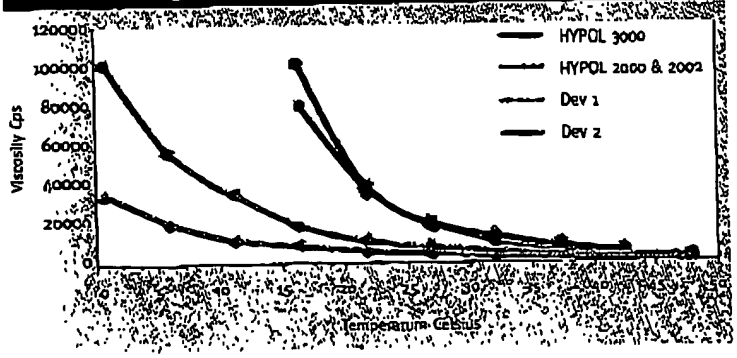
PROPERTY	ASTM METHOD NUM.	HYPOL* 2000 PREPOLYMER	HYPOL* DEV 1 PREPOLYMER	HYPOL* DEV 2 PREPOLYMER
CFD at 25% Kg/cm² (psi)	3574-C	0.16 (2.28)	0.46 (6.53)	0.15 (2.39)
Tensile Elongation (%)	3574-E	473	700	757

TABLE N° 5

PROPERTY	ASTM METHOD NUM.	HYPOL* 2000 PREPOLYMER	HYPOL* DEV 1 PREPOLYMER	HYPOL* DEV 2 PREPOLYMER
Elongation (%)	3574-E	76	594	385

Improved Processing

FIGURE 3. HYPOL* PREPOLYMERS VISCOSITY PROFILE



One of the benefits of the new developmental HYPOL* grades is the lower viscosity profile in comparison to the current HYPOL* 2000, 2002 and 3000 grades as detailed in Figure 3. Additionally, as the new developmental HYPOL* grades exhibit lower viscosity and lower freezing point, lower levels of energy are required for:

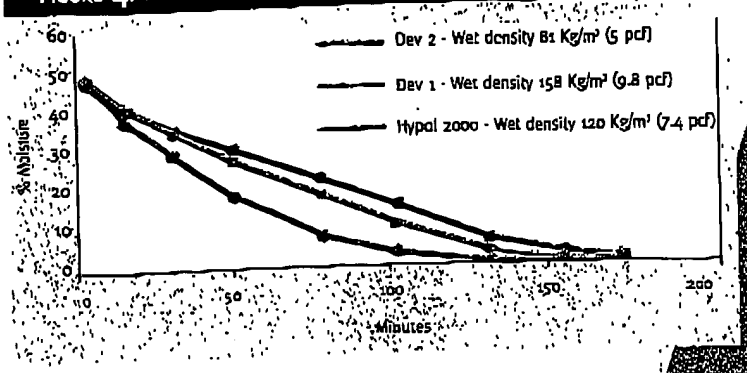
- Conditioning and handling: shorter conditioning cycles prior to use.
- Processing: lower temperatures can be used in the holding tank and transfer lines.

Foams prepared with the HYPOL* Developmental Grades 1 and 2 exhibited a

reduction in the drying cycle, as illustrated in Figure 4, when compared to the foams produced with HYPOL* 2000. Free risen foams were prepared with an initial moisture content of 48 %. Specimens were cut free of skin to the following average dimensions: thickness 1.27 cm (0.5 inch). length 17.78 cm (7 inches) and width 10.16 cm (4 inches). They were placed in a forced convection oven at 70°C (158°F) to dry. The reduction in weight was continuously monitored until the foams were bone dry.
The Moisture Percentage was calculated using the following:

Formula:
% Moisture = (Initial Weight - Final Weight) / Initial Weight

FIGURE 4. DRYING RATE AT 70° CELSIUS FOAM THICKNESS 1.25 CM



Conclusions

The development program established within Dow Polyurethane Systems business, has yielded a new series of developmental grades of hydrophilic prepolymers, HYPOL* DEV 1 and HYPOL* DEV 2.
These new grades, and the foams produced with them, are capable of addressing several of the challenges and restrictions polyurethane hydrophilic foams face today. Among the most important:

- Improved physical properties when wet;
- Lower viscosity and solidification temperature;
- Lower energy levels required for processing of the prepolymer.

Additional hydrophilic grades based on MDI are currently under development.

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